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In situ synthesis of cobalt-based tri-metallic nanosheets as highly efficient catalysts for sodium borohydride hydrolysis

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ABSTRACT

The well dispersed magnetically recyclable tri-metallic nanosheets with non-noble metallic elements have been successfully synthesized via a facile one-step in situ procedure using sodium borohydride ($NaBH_4$) as the reducing agent. The 2-D metal nanosheets exhibit higher catalytic activities for hydrolytic dehydrogenation of $NaBH_4$ than those traditional mono-metallic, bimetallic and trimetallic alloy nanoparticles. The synergetic interaction between Co and Ni in CuCoNi nanosheets may play a critical role in the enhanced catalytic activity. Furthermore, the kinetic studies indicate that the catalytic hydrolysis of $NaBH_4$ by the CuCoNi nanosheets is first order, with the activation energy measured to be 40.6 kJ mol^{-1}.

Introduction

With increasing energy demand, the development of sustainable energy resources is becoming the focus of extensive studies. Hydrogen is considered to be one of the most promising candidates to replace nonrenewable fuel sources used nowadays, owing to its high energy density, zero emission and abundant source [1–7]. But many key challenges need to be addressed towards realizing the prospective hydrogen economy. The most prominent issues are: 1) finding new effective hydrogen-storage materials and 2) efficient catalysts for the hydrogen-release reaction [6,8]. Among various practical hydrogen storage materials, sodium borohydride ($NaBH_4$) has been viewed as one of the leading molecular candidates for hydrogen storage, because of its outstanding physicochemical properties, such as nonflammable, low molecular weight (37.83 g mol^{-1}), high (theoretical) stored hydrogen capacities (10.8 wt%), excellent room-temperature stability in solid form, good stability in neutral and in alkaline aqueous solutions, safe and efficient release of hydrogen through either pyrolysis or hydrolysis routes [9,10]. It can generate hydrogen in the following way:

$$NaBH_4(s) + 2H_2O(l) \xrightarrow{Catalyst} NaBO_2(aq) + 4H_2(g)\uparrow + Heat \quad (1)$$

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However, the hydrogen generation rate of $NaBH_4$ is very slow in the absence of suitable catalysts, which seriously restricts its development as a promising hydrogen storage material. Therefore, it is urgent to synthesize efficient and durable catalysts for the $NaBH_4$ hydrolysis. Usually, owing to the superior catalytic properties towards the hydrolysis of $NaBH_4$, noble-metal catalysts are dominated, such as Ru [2,11,12], Pd [13], Pt [14,15] and Rh [16]. However, noble-metal catalysts have the strong social demand and the high cost, so numerous efforts have been devoted to optimize noble-metal compositions in catalysts and to design new catalysts with less or no noble metals. Up to now, many reports have focused on the bimetallic catalysts, such as Pd–Co [17–19], Pt–Co [20], Ni@Ru [21], while little attention is paid to tri-metallic catalysts. Considering the effect of synergetic interaction among multi-components on the catalytic activity, efforts have been made to synthesize trimetallic catalysts to improve their catalytic activities towards the hydrolysis of $NaBH_4$ [22,23]. Among them, Co-based nanocatalysts have drawn special attention on account of their high catalytic performance and much lower cost compared with noble metal nanoparticles catalysts [1,24–26]. However, supported or unsupported magnetic NPs in the form of powder are likely to aggregate owing to their high surface energy and magnetic attraction between each other, which may lower their catalytic activity and reduce the lifetime of catalysts [27]. In contrast, the 2-D metal nanosheets consisting of anisotropic nano-units are expected to show better catalytic activity than those traditional metal NPs for the $NaBH_4$ hydrolysis [28]. However, in spite of significant advances in the synthetic process of metal nanosheets, tri-metallic nanosheets with non-noble metallic elements have not been reported, to say nothing about their synergistic effects and enhanced performances upon the hydrolysis of $NaBH_4$.

In this study, we report a facile but efficient method to synthesize CuCoNi nanosheets through a one-step synthetic route at room temperature. Furthermore, in contrast to their mono-metallic NPs, bimetallic and tri-metallic alloys, the present CuCoNi nanosheets exhibit the superior catalytic activity and excellent stability to hydrogen generation from hydrolysis of $NaBH_4$. Moreover, the present catalyst, containing two magnetic elements of Co and Ni, is easily separated from the reaction solution during the recycle application.

Material and methods

Material

All chemicals, cobalt (II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99.0%), copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.0%), nickel (II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, 98.0%), sodium borohydride ($NaBH_4$, 97%), and polyvinylpyrrolidone (PVP, K-30, $(C_6H_9NO)_n$), were of analytical grade and were used without further purification.

Synthesis of CuCoNi nanosheets

The CuCoNi nanosheets were synthesized by a facile chemical reduction method. Typically, for $Cu_{0.04}Co_{0.864}Ni_{0.096}$ nanosheets, 40 μL of 100 mM $CuCl_2 \cdot 2H_2O$, 864 μL of 100 mM $CoCl_2 \cdot 6H_2O$ and 96 μL of 100 mM $NiSO_4 \cdot 6H_2O$ was mixed in an aqueous solution of PVP (150 mg, 10 mL). After ultrasonication for 5 min, the solution was introduced into a 50 mL beaker which contains 5 mL of 150 mM $NaBH_4$ (freshly prepared) with stirring for several minutes. The product of CuCoNi nanosheets in a suspension liquid could be directly used for the hydrolytic dehydrogenation of $NaBH_4$ without further treatment.

Keeping the total metal molar amount constant, we can easily obtain other CuCoNi nanosheets with different Cu, Fe and Ni compositions by a similar method shown above. The molar ratio of Co^{2+} to Ni^{2+} was kept as a constant of 1. Simultaneously, the molar ratio of Cu^{2+} to the total number of moles in the metal salts was changed from 0 to 1 to obtain $Cu_x(Co_{0.5}Ni_{0.5})_{1-x}$. Then the molar ratio of Cu^{2+} to the total number of moles in the metal salts was kept as 0.04, and that of Co^{2+} to Ni^{2+} varied from 0 to 1. In this way, $Cu_{0.04}(Co_yNi_{1-y})_{0.96}$ can be received.

Catalytic activity and activation energy measurement

Typically, the above solution was dropped slowly into a two-necked round-bottomed flask containing $NaBH_4$ (25 mL, 150 mM), which connected to one neck through a pressure-equalization funnel. The other neck was connected to a gas burette. The reactions were started when the mixed solution was added to the flask with magnetic stirring. The volume of generated gas was monitored using a gas burette by means of the water displacement method until no hydrogen was generated. The catalytic activities of these catalysts were detected by measuring the hydrogen generation rate. The as-prepared catalysts were washed and filtered three times with distilled water and ethanol absolute, respectively. After the black particles were dried for about 8 h at 223 K in vacuum, the samples were collected for tests. The reactions were also carried out at different catalyst concentrations and temperatures (298–313 K) to study the $NaBH_4$ hydrolysis kinetics.

Characterization

Morphology and microstructure of the synthesized materials were investigated by scanning electron microscopy (SEM) (FEI Quanta 200 FEG, Holand) equipped with an energy-dispersive spectroscopy (EDS) detector and transmission electron microscopy (TEM) (FEI TECNAI G^2 12, Holand). X-ray diffraction (XRD) analysis data from the samples was collected by using a Rigaku D/MAX 2500 v/pc (Japan) diffractometer with Cu Kα radiation. The chemical valences of metals in the catalyst were analyzed by X-ray photoelectron spectroscopy (XPS) (JPS-9010TR, Japan) with an Mg Kα radiation.

Results and discussion

Catalysts structure and morphology characterization

The morphology of the synthesized CuCoNi nanosheets was investigated by SEM and TEM. The SEM images show the sample prepared in the presence of CuCoNi is composed of a large number of thin crumpled nanosheets with a porous

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